Observation of Competing Order in a High-T_c Superconductor with Femtosecond Optical Pulses

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We present studies of the photoexcited quasiparticle dynamics in $Tl_2Ba_2Ca_2Cu_3O_y$ (Tl-2223) using femtosecond optical techniques. Deep into the superconducting state (below 40 K), a dramatic change occurs in the temporal dynamics associated with photoexcited quasiparticles rejoining the condensate. This is suggestive of entry into a coexistence phase which, as our analysis reveals, opens a gap in the density of states (in addition to the superconducting gap), and furthermore, competes with superconductivity resulting in a depression of the superconducting gap.

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In the Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity, which describes the mechanism of conventional superconductivity for conventional metals, electrons form Cooper pairs mediated by the vibrations of the crystal lattice. For the high-temperature superconductors, another possibility exists, namely, Cooper pairing via antiferromagnetic spin fluctuations [1, 2]. Indeed, a full-fledged antiferromagnetic order, out of which such antiferromagnetic fluctuations emerge, can also compete with superconductivity as the dominant ground state resulting in phase coexistence [3, 4, 5, 6, 7]. The coexistence of antiferromagnetic ordering with superconductivity has been observed in single- or double- layer systems in the presence of a magnetic field via neutron scattering [6, 8], or in five-layered systems in zero field using nuclear magnetic resonance [5, 7]. However, it is unclear from these measurements how the emergence of antiferromagnetic order affects the quasiparticle (QP) excitations, which determine the material's optical and electronic response.

An energy gap in the excitation spectrum of a material is of fundamental importance in determining its optical and electronic properties. In superconductors and many other correlated electron materials, many-body interactions open a gap in the QP density of states thereby introducing an additional timescale for the QP dynamics. Independent of its origin, the opening of a gap presents a bottleneck to ground state recovery following photoexcitation of QPs across the gap. The timescale of this recovery is related to the gap magnitude, meaning that interactions which perturb the gap manifest as an easily measured change in the temporal response by monitoring changes in the reflectivity ($\Delta R/R$) or transmission of an interrogating probe beam. In recent years, femtosecond time-resolved spectroscopy has been recognized a powerful *bulk* technique to study temperature-dependent changes of the low-lying electronic structure of superconductors [9] and other strongly correlated electron materials [10, 11, 12]. It provides a new avenue, namely the time domain, for understanding the QP excitations of a material. In this Letter, we present time-resolved studies of photoexcited QP dynamics in the high-T_c superconductor Tl-2223. We observe that its pristine superconducting state (40 K $< T < T_c$) subsequently evolves into a coexistence phase as evidenced by a strong modification of the gap dynamics below 40 K.

Our sample is a slightly underdoped single crystal of Tl-2223 with T_c=115 K, grown by the self-flux method [13]. Tl-2223 is a tri-layered crystal, where its two outer CuO_2 planes has a pyramidal coordination with an apical oxygen, while the inner plane has a square coordination with no apical oxygen. In our experiments an 80-MHz repetition rate Ti:sapphire laser produces 80-fs pulses at $\approx$800 nm (1.5 eV) as the source of both pump and probe optical pulses. The pump and probe pulses were cross-polarized, with a pump spot diameter of 60 μm and probe spot diameter of 30 μm. The reflected probe beam was focused onto an avalanche photodiode detector. The pump beam was modulated at 1 MHz with an acoustic-optical modulator to minimize noise. The average pump power was 300 μW, giving a pump fluence of $\sim$0.01 μJ/cm^2 and a photoexcited QP density of 0.002/unit cell, showing that the system is in the weak perturbation limit. The probe intensity was 10 times lower. Data were taken from 7 K to 300 K. The photoinduced temperature rise at the lowest temperatures was estimated to be $\sim$10 K (in all the data the temperature increase of the illuminated spot has been accounted for). The small spot sizes enable us to use a very small pump fluence without sacrificing signal-to-noise ratio, while keeping sample heating to a minimum and thus enabling data to be taken at low temperatures. The resolution is at least 1 part in 10^6. We also used a 2-MHz repetition rate cavity-dumped laser to obtain data at 7 K.

Figure 1 shows the time dependence of the photoinduced signal of Tl-2223. At high temperatures the signal is characterized by a negative $\Delta R/R$ transient which relaxes within $\tau_n$$\sim$0.5 ps with τ_n decreasing slightly as

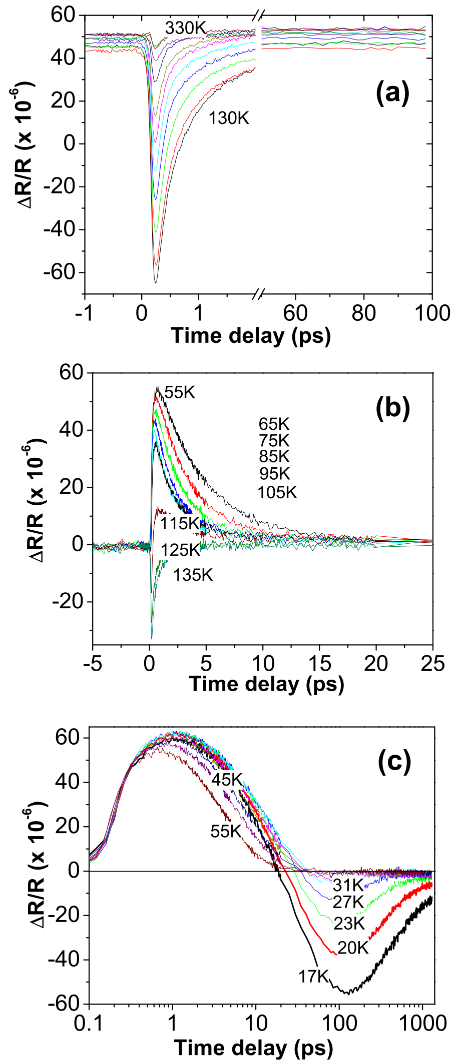

FIG. 1: Photoinduced transient reflection $\Delta R/R$ versus time delay between pump and probe pulses, at a series of temperatures through T_φ and T_c. The logarithmic scale is used for the time-axis in the low-temperature region (Fig. 1c).

temperature is increased to 300 K (Fig. 1a) consistent with QP thermalization in conventional metals [14]. Below T_c, we observe the onset of a positive $\Delta R/R$ with a relaxation time (τ_{SC}) of a few picoseconds due to the opening of the superconducting gap (Fig. 1b). Surprisingly, below ∼40 K, $\Delta R/R$ first goes positive, relaxes to zero with a lifetime τ_{SC}, *then crosses zero and goes negative*, before relaxing back to equilibrium over a time scale of a few hundred picoseconds (Fig. 1c). We ascribe the short-decay positive signal to the reformation of superconducting order following photoexcitation, and the *long-decay negative signal to the development of a new competing order other than superconductivity*. We define the second transition temperature as T_φ. Accordingly, we fit the data of $\Delta R/R$ in different temperature ranges as follows: In the normal state ($T > T_c$), the data follow $\Delta R/R = B_0 + B_n \exp(-t/\tau_n)$, where $B_n < 0$; in the phase with only the superconducting order parameter ($T_\varphi < T < T_c$), the data follow $\Delta R/R = A_0 + A_{SC} \exp(-t/\tau_{SC})$, where $A_{SC} > 0$; in the coexistence region, ($T < T_\varphi$), the data follow $\Delta R/R = A_0 + A_{SC} \exp(-t/\tau_{SC}) + A_\varphi \exp(-t/\tau_\varphi)$, where $A_{SC} > 0$ and $A_\varphi < 0$. Figure 2 shows the temperature-dependence of the peak amplitudes $A_{SC}(T)$, $A_\varphi(T)$ and $B_n(T)$. We see that below ∼40 K, A_φ increases from zero, while A_{SC} exhibits a sharp kink.

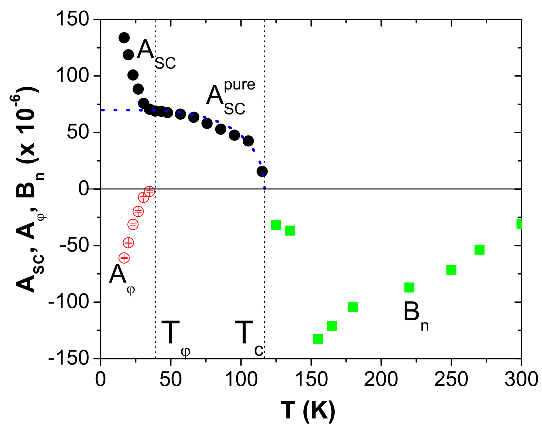

FIG. 2: Temperature dependence of the peak amplitudes. Solid circles: A_{SC}. (O): A_φ. Solid squares: B_n. Dotted line: BCS fit to A_{SC} in the temperature range $T_\varphi < T < T_c$, extrapolated to T=0.

We use the Rothwarf-Taylor (RT) model to explain our data [15]. It is a phenomenological model used to describe the relaxation of photoexcited superconductors, where the presence of a gap in the electronic density-of-states gives rise to a bottleneck for carrier relaxation. When two QPs with energies $\geq \Delta$ recombine (Δ is the superconducting gap magnitude), a high-frequency boson (HFB) with energy $\omega \geq 2\Delta$ is created. The HFBs that remain in the excitation volume can subsequently break additional Cooper pairs effectively inhibiting QP recombination. Superconductivity recovery is governed by the decay of the HFB population. The RT analysis for a material with a single energy gap, is as follows [16]: from the temperature-dependence of the amplitude A, one obtains the density of thermally excited QPs n_T via $n_T \propto A^{-1} - 1$, where $A(T)$ is the normalized amplitude $[A(T) = A(T)/A(T \to 0)]$. Then we can fit the n_T-data to the QP density per unit cell

$$n_T \propto \sqrt{\Delta(T)T} \exp(-\Delta(T)/T), \tag{1}$$

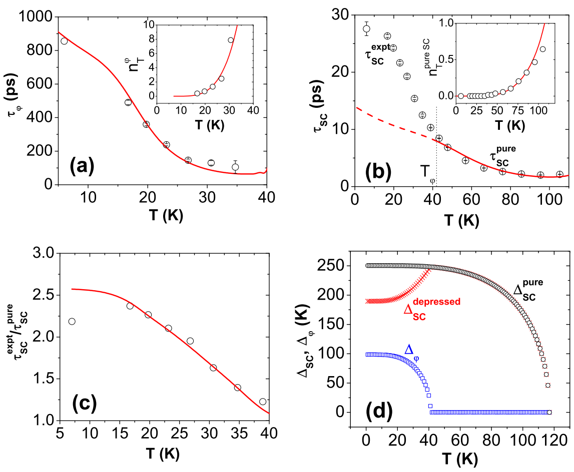

FIG. 3: Temperature dependence of relaxation times τ and thermally-excited QP densities n_T. (a) $\tau_\varphi(T)$ and $n_T(T)$ of the competing order component. Solid curves are fits using the RT model. (b) $\tau_{SC}(T)$ and $n_T(T)$ of the superconducting component. Solid curves are fits using the RT model. The RT model fit to $\tau_{SC}(T)$ is only for $T_\varphi < T < T_c$ (solid line). The dashed line is the extrapolation of that fit below T_φ. (c) Experimental values (O) and theoretical fit (solid line) of the ratio $\tau_{SC}^{expt}/\tau_{SC}^{pure}$. (d) Superconducting gap $\Delta_{SC}(T)$ with and without suppression, and the gap $\Delta_\varphi(T)$ due to the competing order, using the Ginzburg-Landau theory.

with $\Delta(0)$ as a fitting parameter and $\Delta(T)$ obeying a BCS temperature dependence. Moreover, for a constant pump intensity, the temperature dependence of n_T also governs the temperature-dependence of the relaxation time τ, given by [16, 17]

$$\tau^{-1}(T) = \Gamma[\delta + 2n_T(T)](\Delta + \alpha T \Delta^4), \tag{2}$$

where Γ, δ and α are temperature-independent fitting parameters, with α having an upper limit of $52/(\theta_D^3 T_{min})$, θ_D being the Debye temperature and T_{min} the minimum temperature of the experiment.

We first consider the competing component below T_φ. In this regime we have two types of ordering — the competing and superconducting order. Since the nature of the competing order is unknown *a priori*, we assume that its formation opens an isotropic QP gap (we discuss the microscopic nature of the competing order below). Therefore, the bottleneck effect is mostly dominated by this new gap. We then fit the data for the new order (A_φ and τ_φ) using the RT model described above. That is, from $A_\varphi(0)$ and $A_\varphi(T)$, we obtain n_T (circles in the inset of Fig. 3a). Then we fit $n_T(T)$ with Eq. 1 (solid line in the inset of Fig. 3a) using the gap values $\Delta_\varphi(T)$ obtained from Ginzburg-Landau theory shown in Fig. 3d. Finally, we insert the fitted values of $n_T(T)$ into Eq. 2 to determine the experimental values of τ_φ, as shown in Fig. 3a.

The excellent fit lends strong support to our assumption of the opening of a QP gap upon the development of the competing order. The dynamics of this competing order can be explained by a relaxation bottleneck associated with the presence of a gap in the density of states.

Next we turn to the superconducting component. In the range $T_\varphi < T < T_c$, with only one order parameter in the system, namely superconducting order, we fit the data to the single-component RT model described above, where recombination occurs only from the superconducting energy gap. The signal amplitude is labelled $A_{SC}^{pure}(T)$, with the superscript denoting the pure superconducting component without the existence of a competing order. $A_{SC}^{pure}(T=0)$ is not the experimental value shown on Fig. 2, but is that extrapolated from $A_{SC}^{pure}(T > T_\varphi)$, via the BCS temperature dependence, assuming that the competing order does not exist. This is shown as a dashed line on Fig. 2, whence one obtains $A_{SC}^{pure}(T=0) \approx 70.0 \text{ x } 10^{-6}$. From $A_{SC}^{pure}(0 < T < T_c)$ one then obtains $n_T^{pureSC}(T)$ as shown in the inset of Fig. 3b (circles), where the fit to Eq. 1 yields $\Delta(0) = 2.14\mathrm{k}_B T_c$ (solid line), in agreement with the typical *d*-wave value. Again, using these fitted values of $n_T^{pureSC}(T)$, one fits the experimental values of $\tau_{SC}^{pure}(T)$ in the range $T_\varphi < T < T_c$ using Eq. 2, shown on Fig. 3b. Similar to the competing phase above, the relaxation dynamics of the pure superconducting phase can also be explained by the presence of a relaxation bottleneck due to a (superconducting) gap in the density of states.

We immediately notice from Fig. 3b that below T_φ, the fitted values $\tau_{SC}^{pure}(T)$ (dashed line) underestimate the experimental values. In the Ginzburg-Landau theory [18], the coupling between the competing and superconducting order parameters causes the superconducting gap to be suppressed. Hence the superconducting energy gap Δ_{SC} decreases below its BCS value, as shown in Fig. 3d. Since at a fixed temperature, τ increases as Δ decreases (and vice versa) [10], we can infer that, below T_φ, the increase of the experimental relaxation time $\tau_{SC}^{expt}(T)$ over its BCS value $\tau_{SC}^{pure}(T)$ is due to the suppression of the superconducting gap in this temperature range. From Eq. 2, we can more accurately put

$$\frac{\tau_{SC}^{expt}}{\tau_{SC}^{pure}} \propto \frac{\Delta_{SC}^{pure} + \alpha T (\Delta_{SC}^{pure})^4}{\Delta_{SC}^{suppressed} + \alpha' T (\Delta_{SC}^{suppressed})^4}, \tag{3}$$

where α is obtained earlier from the fit to $\tau_{SC}^{pure}(T)$, and α' is a fitting parameter. Figure 3c shows the ratio $\tau_{SC}^{expt}/\tau_{SC}^{pure}$ (circles), and the fit given by Eq. 3 (solid line). We see that the fit reproduces the general shape of $\tau_{SC}^{expt}/\tau_{SC}^{pure}$ — an increase below 40 K and flattening out around 15 K. Our analysis shows that the deviation of A_{SC} and τ_{SC} from the BCS temperature dependence below T_φ is due to the *depression* of the superconducting gap, which is caused by the appearance of the second order. It confirms the *competing* nature of this new order

below T_φ.

Our work is unique compared to other techniques in various aspects. First, we see the coexistence phase in zero field, while neutron scattering data on $La_{2-x}Sr_xCuO_4$ and $Nd_{1.85}Ce_{0.15}CuO_4$ sees the emergence of the antiferromagnetic phase only with an externally applied magnetic field [6, 8]. Thus our data are not complicated by the presence of vortex lattice and/or stripe order. Second, this is the first observation of the coexistence phase using ultrafast spectroscopy, a tabletop setup compared to large facilities required for neutron scattering experiments. Third, our technique only requires a sample volume of $\sim10^{-10}$ cm^3 (due to a small laser spot diameter of 60 μm and skin depth in the cuprates of $\sim$80 nm), which is orders of magnitude smaller than that in neutron scattering ($\sim$1 cm^3). This makes our technique especially suitable for ultrathin platelet-like samples such as the cuprates, enabling us to probe a much wider class of cuprate superconductors. Fourth, a tri-layered cuprate system has the highest T_c in a homologous series, and as compared to other members with a higher number of layers, has the closest charge distribution between the outer and inner CuO_2 planes and exists in a single phase [19]. Ours is the first observation of the coexistence of a competing order with superconductivity in a tri-layered system. Fifth, we have successfully applied the RT model to systems with more than one gap in the density of states, where we *quantified* the reduction of the superconducting gap in the presence of a competing order. Though our technique cannot determine whether this new order is magnetic or not, our data clearly show that it *competes* with superconductivity. The emergence of this new order opens a QP gap, and our data can be fit excellently with a BCS-like gap, indicating the new order is not inconsistent with a commensurate antiferromagnetic spin-density-wave as revealed in zero-field NMR data on five-layered polycrystalline cuprates [5, 7]. However, we do not exclude the possibility that the competing order can be *d*-density wave order [20], circulating current order [21], or charge density wave order [22]. Contrast this coexistence phase at zero field in multi-layered samples with the situation in single-layered cuprates, where at a finite hole doping only a single superconducting phase exists and the competing phase must be induced by an external perturbation such as dc magnetic field. A possible reason is that for multi-layered cuprates, the competing and superconducting order may nucleate on different planes, with each of their correlation lengths much larger than the interlayer distance, such that the two orders can penetrate into each other even at zero magnetic field. It is precisely the ability of ultrafast spectroscopy to *temporally* resolve the dynamics of different degrees of freedom that enables us to observe these two orders in the coexistence phase.

We took data on another underdoped sample of Tl-2223 with a higher T_c of 117 K, obtaining a lower T_φ of 35 K. This is consistent with the phase diagram of multi-layered cuprates as depicted in Fig. 4 of Ref. 7, where in the (underdoped) coexistence region, the antiferromagnetic transition temperature T_N decreases with increasing doping. Moreover, our recent data on the two-layered cuprate Tl-2212 do not show the zero crossover. This is consistent with ultrafast relaxation data on other one- and two-layered cuprates [9, 23, 24] where the coexistence phase is not expected to exist, showing that our observation of the zero crossover in Tl-2223 is intrinsic and not an artifact of our experimental setup.

Our work presents the first ultrafast optical spectroscopy probe of the coexistence phase in a multi-layered cuprate superconductor where, in zero magnetic field, a new order competes with superconductivity. This competing order is intrinsic to the material and is not induced by any external applied field. The competing order opens up a QP gap, consistent with a commensurate antiferromagnetic order. Our study once again points to the unique characteristic that high-temperature superconductivity results from the competition between more than one type of order parameter. It provides an insight into the mechanism of strongly correlated superconductivity — the quantum fluctuations around this competing order might be responsible for gluing the electrons into Cooper pairs. Theoretical work to solve the RT model in the presence of multiple gaps, as well as experimental studies on other multi-layered cuprates, are clearly needed to elucidate the temporal dynamics of the coexistence phase in high-T_c superconductors.

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